XeF^+, $IF^{+\cdot}$, and Other Unusual Ions Generated by Reactions of Hyperthermal Ion Beams at Self-Assembled Monolayer Surfaces

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Collisions of atomic and molecular ions (I^+, Xe^+, CH_3I^+, $I_2^{+\cdot}$) with self-assembled fluoroalkyl-monolayer surfaces result in reactions involving the net transfer of fluorine atoms or fluorocarbon radicals from the surface to the projectile ions. The scattered products, which include unusual ionic species such as $IF^{+\cdot}$, IF_2^+, $CFI^{+\cdot}$, CF_2I^+, I_2F^+, and XeF^+, are generated in endothermic ion–surface reactions. These reactions are not observed when the collision partner is a gas-phase (rather than a surface-bound) perfluoroalkane. Evidence is presented which suggests that in some cases molecular projectiles undergo surface-induced dissociation to yield atomic species which subsequently react with the surface. Fluorine abstraction is favored for projectiles containing highly polarizable elements. *(J Am Soc Mass Spectrom 1993, 4, 938–942)*

Collisions with surfaces are used to excite and dissociate polyatomic ions in the surface-induced dissociation (SID) experiment [1]. This inelastic collision process is of interest as an alternative to gaseous collisions for structural studies by mass spectrometry [2–6]. Reactive scattering can accompany inelastic scattering when molecular adsorbates or covalently bound organic species are present on the surface. Abstraction of a hydrogen atom or alkyl radical is a common reaction observed upon collisions of open-shell ions at adsorbate-covered metal surfaces [7]. Similar products are formed in ion–surface reactions involving thiol-bound alkyl self-assembled monolayer (SAM) surfaces [8, 9] and single crystal surfaces bearing adsorbed pyridine [10]. Chemical sputtering products [11] consisting of ionized surface adsorbates or their fragments are often observed along with the SID and ion–surface reaction products.

SAM surfaces have been shown to be well ordered [12], and functional groups attached to the terminus provide a means for studying the role of the target surface in ion–surface collisions [13–15]. Perfluorinated surfaces have been compared with the corresponding hydrocarbon surfaces and have been shown to provide greater SID efficiency, to result in more effective translational-to-internal energy conversion, and to be less reactive toward hydrocarbon ion projectiles [13, 15]. Collisions with perfluorinated surfaces have been shown to include at least one ion–surface reaction channel, that involving pick-up of a fluorine atom [13, 15].

Scheme I illustrates several of the processes that occur upon low-energy ion–surface collisions. The lower portion shows a previously proposed mechanism [8, 13] for ion–surface reactions. As discussed earlier [8, 13], many ion–surface reactions appear to be initiated by electron-transfer from the surface to the incoming projectile, M_1^+. The resulting ionized, surface-bound molecule may be formed with excess internal energy, in which case it will undergo fragmentation. The surface-derived fragment, Y^+, can then bind to the neutralized projectile, M_1, to form the ion–surface reaction product, M_1-Y^+. This product itself may undergo subsequent fragmentation if generated with sufficient internal energy. Scheme I illustrates that three of the major ion–surface collision processes, neutralization, chemical sputtering, and ion–surface reaction, may all be interrelated via a common mechanism involving electron-transfer as the first step [1, 11]. Evidence for the electron-transfer mechanism is provided by a number of general trends observed for systems in which organic ions collide with surfaces bearing organic species: (1) the threshold collision energies for ion–surface reactions are often similar to those for chemical sputtering, which is also presumed [11] to involve charge exchange between the surface and projectile as the initiating step; (2) the products of chemical sputtering are often the same as, or similar to, the chemical entities incorporated into the projectile ion during ion–surface reactions; and (3) projectiles with low ionization energies (IE) often exhibit low cross-sections for both reactive collisions and

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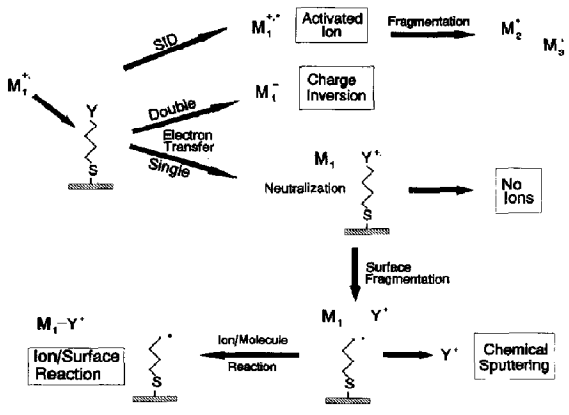
1044–0305/93/$6.00

Received June 2, 1993
Revised August 2, 1993
Accepted August 3, 1993



Scheme I

chemical sputtering [16], and high cross sections for SID which proceeds without electron-transfer.

Here we present results obtained upon collisions of some iodine-containing ions at SAM surfaces of the structure $CF_3(CF_2)_{11}(CH_2)_2$-S-Au and attempt to reconcile the results with the prior mechanistic generalizations. Unlike hydrocarbon projectile ions, iodine-containing projectiles produce a variety of product ions in large abundance formed as the result of ion–surface reactions. The rich surface chemistry resulting from the iodine-containing projectiles colliding with the fluorinated target is the subject of this investigation.

Experimental

The ion–surface collision experiments were performed by using a BEEQ (B = magnetic sector, E = electric sector, Q = quadrupole mass filter) instrument in which the collision surface is located between the two electric sectors [17]. The incident and scattering angles were fixed at 55° and 90°, respectively, for all experiments. Sample vapor was introduced into the ion source via a leak valve, and source pressures ranged from 5×10^{-6} to 1×10^{-5} torr, depending on the compound. Ions were formed by 70 eV electron ionization (EI), and the parent ion was selected with unit mass resolution using the first two sectors (BE) to produce an ion current of $\approx$ 1 nA at the target surface. Ions scattered from the surface were transmitted through the electric sector, which was set to pass low energy ions, and mass analyzed using the quadrupole mass filter. The SAM surfaces were rinsed three times with hexane (mixture of isomers, Baker Chemical Co., Phillipsburgh, NJ) before being introduced into the scattering chamber, which was held at a pressure of 4×10^{-9} torr. The preparation and characterization of the SAM surfaces are described elsewhere [12, 13].

Analogous experiments, in which the collision partner was a gas-phase rather than a surface-bound fluorocarbon, were performed using a triple quadrupole mass spectrometer (TSQ 700, Finnigan MAT, San Jose, CA). Sample vapor was introduced via a leak valve and ions were produced by 70 eV EI. Mass selected ions of interest were collided with gaseous perfluorohexane (Lancaster Chemical Co., Windham, NH) in the collision quadrupole. Experiments were performed by using a number of laboratory collision energies and pressures, ranging from 1 to 50 eV and 0.6 to 1.4 mtorr, respectively. Product ion spectra were recorded by scanning the third quadrupole.

Neutral precursors for the various projectile ions were: iodomethane (EM Industries, Inc., Cherry Hill, NJ) for the production of CH_3I^+, CH_2I^+, and I^+; and iodine (Baker Chemical Co.) for the production of I_2^+. The xenon (99.95%) was obtained from AIRCO Gases (Murry Hill, NJ).

Results and Discussion

Figure 1a displays the product ions scattered from a fluorinated alkyl SAM surface upon collision of I^+ at 30 eV. The main component of the scattered ion beam is I^+, but the second most abundant signal is due to an ion of m/z 146, assigned as IF^+. This remarkable process requires the cleavage of a C-F bond and formation of an I-F bond. This interfacial reaction is estimated to be $\approx$ 58 kcal/mol (2.5 eV) endothermic by

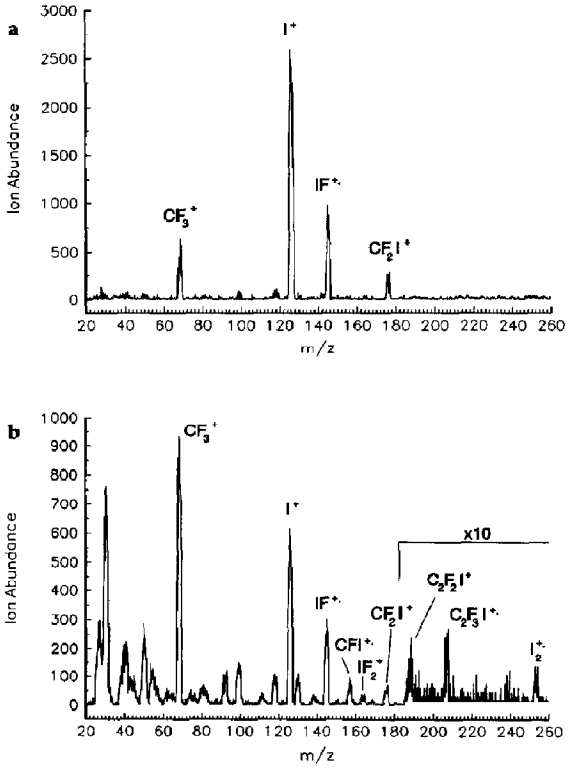


Figure 1. Ion–surface collision products resulting from I^+ impinging upon a fluoroalkyl SAM surface at (a) 30 eV and (b) 60 eV.

using thermodynamic data [18, 19] for the gas-phase process: $I^+ + C_3F_8 \rightarrow IF^{+\cdot} + C_3F_7$. The reaction, therefore, must be driven by the translational energy of the projectile ion. Consistent with this, the reaction was studied as a function of the projectile collision energy and was found to be observable only above 20 eV. The formation of $IF^{+\cdot}$ was observed at collision energies as high as 70 eV, although no attempt was made at finding a high energy limit for the formation of this product.

Surface C-C bond cleavage is responsible for two other major products in the spectrum; CF_2I^+, which again must involve reactive scattering, and CF_3^+, which is the result of chemical sputtering [11]. As the collision energy is increased to 60 eV (Figure 1b), a number of additional product ions appear in the spectrum, pointing to the complexity of the phenomena taking place at the surface. The main products of ion–surface reactions are summarized in Table 1. Several of these ions, such as IF^+, IF_2^+, and CF_2I^+, are unusual chemical species, whereas others, such as CFI^+, have rarely been reported. Furthermore, no reports could be found demonstrating the formation of these species via analogous endothermic gas-phase reactions, and experiments (described below) in which the same projectiles collided with gaseous perfluorohexane produced no ion–molecule reaction products under a variety of experimental conditions. This emphasizes the unique conditions that prevail during ion–surface collisions which, as shown here, allow cleavage of strong covalent bonds and incorporation of groups from the surface into the ionic projectile, resulting in the formation of fairly high energy, weakly bound species.

Table 1. Product ions resulting from collisions of iodine-containing projectiles upon the fluorinated surface (60 eV collision energy)[a]

Product Ion	*m/z*	I^+	$CH_3I^{+\cdot}$	$I_2^{+\cdot}$
CH_2F^+	33		20	
$C_2H_2F^+$	45		7	
CHF_2^+	51		14	
I^+	127	100	100	100
$CH_3I^{+\cdot}$	142		138	
$IF^{+\cdot}$	146	45	34	35
$CFI^{+\cdot}$	158	15	4	6
$CHFI^+$	159		2	
CH_3IF^+	161		8	
IF_2^+	165	5	3	2
CF_2I^+	177	8	9	13
$C_2F_2I^+$	189	2	1	1
$C_2F_3I^+$	208	4	1	2
$C_2F_4I^+$	227	+	+	+
$C_3F_4I^+$	239	+	+	+
$I_2^{+\cdot}$	254	*	*	30
I_2F^+	273			4

[a] Relative abundances are given with respect to I^+.
+ Ion abundance < 1%.
* The ion with *m/z* 254 corresponds to $I_2^{+\cdot}$. In the case of the I^+ and $CH_3I^{+\cdot}$ projectiles, it originates from neutralization and deposition of the I at the surface. The I atoms at the surface can subsequently be picked up by iodine-containing projectiles to form $I_2^{+\cdot}$. The dose dependence of this process was examined to confirm that the source of I on the surface is the impinging beam itself. These results will be reported elsewhere.

Other peaks appearing in the spectrum, but not listed in Table 1, are the result of chemical sputtering, viz. ionization of the surface and release of secondary ion fragments including CF_3^+ (*m/z* 69), $CF_2^{+\cdot}$ (*m/z* 50), $C_2F_4^{+\cdot}$ (*m/z* 100), and $C_2F_5^+$ (*m/z* 119). The presence of some hydrocarbon adsorbate is indicated by a series of ions at *m/z* 27, 29, 39, 41, and 55. These hydrocarbon ions could arise from adventitious hydrocarbons on the surface [7], or from the ion beam striking the stainless-steel target holder carrying adsorbate. Note that although sputtering and ion–surface reactions change the target surface, the spectra are not time-dependent under the conditions used, and they were reproducible when the same surface was used over a period of many hours.

To investigate the underlying processes, the reactions of molecular projectile ions containing iodine were studied. Both $CH_3I^{+\cdot}$ and $I_2^{+\cdot}$ yielded results similar to those of the atomic iodine projectile (Table 1). The fact that bond cleavage accompanies bond formation adds to the complexity of these spectra, and most of the observed ion–surface reaction products of the polyatomic projectiles may be formed by more than one route. For example, one possibility for $IF^{+\cdot}$ formation from the $CH_3I^{+\cdot}$ projectile is through the CH_3IF^+ ion (also observed in the mass spectrum, Table 1), which might fragment by loss of methyl to yield $IF^{+\cdot}$. However, molecular beam studies show that the EI mass spectrum of $CH_3IF^{\cdot}$ yields $CH_2IF^{+\cdot}$ as a major fragment [20], and this ion is not observed here. A second possibility is that the $IF^{+\cdot}$ ion results from an ion–surface reaction in which intermediates, such as $CF_3I^{+\cdot}$ or $C_2F_5I^{+\cdot}$, are formed with excess internal energy and subsequently fragment. This route is unlikely because photoelectron photoion coincidence studies indicate that neither $CF_3I^{+\cdot}$ nor $C_2F_5I^{+\cdot}$ fragments to give $IF^{+\cdot}$ [21]. Consequently, it appears that $IF^{+\cdot}$ is formed through initial fragmentation of $CH_3I^{+\cdot}$ at the surface to yield an atomic iodine species (which may, but need not, be charged; see discussion below) followed by addition of fluorine from the surface to yield $IF^{+\cdot}$. Note that the $IF^{+\cdot}$ signal does not vary with time in the ion-dose range used here, suggesting that dissociation and reaction occur in the same collision sequence.

Many of the same product ions are formed from different iodine-containing projectiles (Table 1), and this provides further support for a mechanism involving projectile fragmentation followed by reaction. The near equal ratio of abundances of all of the product ions, irrespective of the nature of the projectile, bears this out. Except for the CH_3IF^+ ion and a low abundance $CHIF^+$ ion, none of the products of the $CH_3I^{+\cdot}$ projectile above *m/z* 142 contain hydrogen, suggesting that $(M + CF_3)^+$ or $(M + C_2F_5)^+$ are unlikely intermediates in the formation of the observed ions and supporting their formation by reaction of the iodine frag-

ment. Finally, the collisions of CH_2I^+ at the fluorinated surface have also been examined. The fact that this ion does not show the addition of fluorine to form CH_2IF^+, and yet yields IF^+, CFI^+, IF_2^+, and CF_2I^+ products, is in agreement with the fragmentation followed by reaction sequence proposed above.

The mechanism described in the Introduction which involves electron-transfer was based on data from the reactions of hydrocarbon ions with hydrocarbon surfaces. The systems studied here, namely halide containing projectile ions colliding with a fluorinated surface, are chemically quite different, yet their behavior is similar to that of the hydrocarbon-ion/hydrocarbon-surface systems in that sputtering and ion–surface reactions exhibit similar collision energy thresholds. On this basis, it seems likely that the reactions of the halide containing ions with the fluorinated surface are also initiated by electron-transfer. However, an alternative mechanism, in which the projectile ion or its ionic fragment directly abstracts a fluorine radical from the surface, must also be considered. Somogyi et al. [15] have suggested such a mechanism for F atom pick-up by the benzene molecular ion, on the basis of thermochemical considerations. In addition, recent studies in which metal ions pick up multiple fluorine atoms suggest that mechanisms involving direct atom abstraction from the surface without electron-transfer may occur in some cases (unpublished study from this laboratory).

Although iodine cations and iodine-containing molecular ions undergo reactive collisions with fluoroalkyl surface groups, the corresponding bromine-containing ions are much less reactive, and those containing chlorine are virtually unreactive. The experimentally measured ratios of scattered-to-impinging beam intensity indicate that $CH_3Cl^{+\cdot}$ (IE = 11.22 eV) and $CH_3Br^{+\cdot}$ (IE = 10.54 eV) undergo charge exchange more readily than $CH_3I^{+\cdot}$ (IE = 9.54 eV). However, $CH_3I^{+\cdot}$ is more reactive, either because its reaction does not involve charge exchange or because the formation of the $XF^{+\cdot}$ interhalogen products from the corresponding $CH_3X^{+\cdot}$ projectiles is less endothermic in the case of iodine [18, 19]. The larger number of states in $CH_3I^{+\cdot}$ might also increase the probability of successful curve crossing and, moreover, at a fixed collision energy, the heavier projectiles will move more slowly, further enhancing the possibility of curve crossing required for electron-transfer and, in addition, increasing the probability of subsequent bond-forming reactions.*

To test further the idea that these remarkable endothermic ion–surface reactions are facilitated by large polarizable atoms, reactions of $Xe^{+\cdot}$ were explored. Figure 2 shows the formation of XeF^+ as a result of bombarding the fluorinated SAM surface with $Xe^{+\cdot}$ ions. This system is of additional interest because the process involves cleavage of a strong C-F bond and generation of a weak Xe-F bond. The fact that I^+ and $Xe^{+\cdot}$ react analogously and so unexpectedly emphasizes the uniqueness of these ion–surface reactions, and the formation of this rather weakly bound product emphasizes the role of the surface in removing excess energy. Production of XeF^+ is very sensitive to the kinetic energy of the $Xe^{+\cdot}$ projectile. Maximum intensity for this product is obtained at a collision energy of 40 eV and its abundance falls off rapidly as the collision energy is changed by 10 eV in either direction. The overall reaction is estimated to be 75 kcal/mol (3.2 eV) endothermic,† while postcollision kinetic energy measurements [13] on the scattered ions show that the ions leave the surface with 10 ± 5 eV of translational

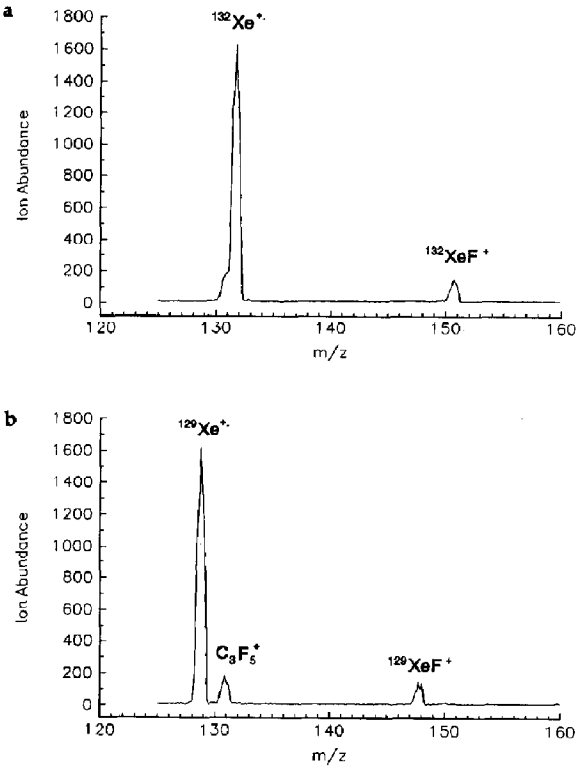


Figure 2. Mass spectra showing the formation of XeF^+ resulting from collisions of **(a)** $^{132}Xe^{+\cdot}$ and **(b)** $^{129}Xe^{+\cdot}$ with the fluorinated SAM surface at an energy of 40 eV. The $C_3F_5^+$ ion, which results from sputtering, is obscured in spectrum **a** and appears as a shoulder on the $^{132}Xe^{+\cdot}$ peak.

* Exothermic and thermoneutral ion–molecule reactions have cross-sections which fall with relative velocity; endothermic reactions have much smaller cross-sections which maximize at nonzero relative velocities. Little is yet known of the situation at the surface, but the additional reaction time made available by a slower projectile may be important. If a reaction zone extending 0.5 nm from the surface is considered, then a 30 eV ion of mass 35, for example, Cl^+, spends 0.60 ps on a single pass through the zone, while the I^+ ion spends 1.2 ps. Both carry the same excess energy with which to surmount any endothermicity barrier.

† This value is based on ΔH for the reaction $Xe^{+\cdot} + C_3F_8 \rightarrow XeF^+ + C_3F_7$. Thermochemical data taken from refs 18 and 19.

energy. Hence, the remaining 20 to 30 eV of the projectile ion's initial kinetic energy must be efficiently deposited into the surface, or emitted radiatively to allow survival of the relatively fragile XeF^+ species (bond energy = 47 kcal/mol = 2.0 eV) [18]. Collisions of $Kr^{+\cdot}$, $Ar^{+\cdot}$, $Ne^{+\cdot}$, and $He^{+\cdot}$ at the fluorinated surface do not result in fluorine atom addition products, further supporting the suggestion that heavy, polarizable atoms with a large number of states are most likely to undergo this type of reaction. Consistent with this, $W(CO)_6^{+\cdot}$ is observed to yield small amounts of $W(CO)_nF^+$ (n = 1,2) when scattered from the fluorinated SAM surface [13].

To explore the possibility that the observed ion–surface reactions may have gas-phase analogs, experiments were performed in which $CH_3I^{+\cdot}$, I^+, and $Xe^{+\cdot}$ collided with gaseous perfluorohexane in a triple quadrupole mass spectrometer at collision energies ranging from 1 to 50 eV and pressures ranging from 0.6 to 1.4 mtorr. No significant ion–molecule reaction products were observed, while fragments arising from ionized target gas accounted for much of the observed signal.

A fascinating area of chemistry is revealed through these investigations in which strong bonds are broken and unusual chemical entities are formed in hyperthermal collisions at surfaces. The evidence indicates that reaction can follow fragmentation, suggesting that this may be the result of a direct scattering process [22] but not necessarily one which involves only a single microscopic collision event. Nevertheless, as a minimum, the lack of a dose dependence in the cases examined suggests that projectiles deposited at the surface are not involved in the reactions reported here, and that a single collision sequence is involved. Some questions remain unanswered, including (1) how much time the ions spend at the surface and (2) whether the reactions are initiated by long-range electron-transfer. Further insights are being sought through measurements on the kinetic energies and angular distributions of the scattered products.

Acknowledgments

This work was supported by the National Science Foundation (CHE-9223791). The self-assembled monolayer surfaces were prepared by Matt Linford and Professor Christopher Chidsey at Stanford University. The assistance of Jeff Patrick and Steve Hoke is gratefully acknowledged.

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